Time-Dependent Ising Model Description[*]
of Binary Liquid Mixture

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Phase transitions are not only characterized by singularities in thermodynamic derivatives, but also by peculiarities in the time-dependent behavior of the system. By employing a time-dependent generalization of the Ising model and a master equation, the relaxation of a local deviation from equilibrium for a system near its critical temperature, is described. Approximate solution of the equations yield results in agreement with recent optical experiments, in which the decay of concentration fluctuations in critical mixtures of liquids is measured; results are also consistent with N.M.R. measurements in anti-ferromagnets. If the equations are solved more accurately, however, it is found that the decay of a local displacement from equilibrium concentration in the critical region is in general not describable by a single exponential.

INTRODUCTION

The Ising model is best-known as a simple many-body Hamiltonian, which if inserted into the partition function, leads to a description of the critical behavior of various physical systems: Ferromagnets, anti-ferromagnets, liquid-vapor systems, binary liquid mixtures, binary alloys. For the two-dimensional Ising model, the partition function can be evaluated exactly[1]; while for the three-dimensional Ising model only approximate and series expansion methods exist.[2] There may thus be two types of approximations involved in applying the Ising model, viz. a) the replacement of the physical Hamiltoniam by the model Hamiltonian, and b) approximations made (if any) in evaluating the partition function.

The only undetermined parameter in the theory is the lattice spacing. The exact two-dimensional calculation is particularly significant, because it verifies the notion [3] that a phase transition and critical behavior can be rigorously derived from the Hamiltonian of a many-body system via the partition function and equilibrium statistical mechanics.

Recently reported experiments yield quantitative information about the rate at which fluctuations near the critical point decay. Such experiments have been carried out in binary liquid mixtures,[4] in anti-ferromagnetic solids[5], in liquid-vapor systems[6] and in ferromagnets.[7] Most of the experiments[8] show very slow decay rates near the critical point, roughtly proportional to ($T - T_c$), as the critical temperature is approached from above. Not unrelated is the well-known experimental fact, that near T_c most systems seem to take a very long time to come to thermal equilibrium. A simple phenomenological theory, based on the diffusion equation, has been given for the binary liquid experiments by Debye.[9] Phenomenological theories also exist for the other experiments mentioned.[10] [11] [8]

These theories are consistent with most of the experimental results.[8]

The purpose of the present paper is to formulate a theory of the relaxation of a generalized Ising model Hamiltonian [12] [13] [14] ,which can be applied to the description of time-dependent phenomena ,in the critical region. It will be applied, for the sake of being explicit and specific, to concentration-fluctuations of a binary liquid mixture, for which the liquids are completely miscible above T_c, but not below T_c. Such a theory is very different from a phenomenological theory because a) it begins with an explicit miscroscopic description of the system and b) instead of the near-equilibrium, slowly-varying and linearity assumptions of the phenomenological theories, rather different assumptions are made. The assumptions of the phenomenological theories would not be expected to be valid for short wave-length, i.e. large scattering angle, while this limitation does not appear in the present formulation. A more important difference is that according to the present formulation, the rigorous calculation of relaxation times near and also below T_c would depend on higher order correlation functions, which are ignored from the outset in the phenomenological theories.

The chief reason for pursuing the Ising-model approach is that one would like to obtain results based on a detailed microscopic picture. The approximations entering into the theory may be seen against the back-drop of the assumptions entering into the use of the Ising model in equilibrium statistical mechanics. The approximations and assumptions we shall make, are: a) the replacement of the physical Hamiltonian by a model Hamiltonian, b) the use of a master equation [13] [14] to calculate the probability that the system is in a particular state, and c) approximations in solving the master equation. The different states, whose occupation probabilities emerge from the master equation, are the eigenstates of an

Ising model Hamiltonian. The transition probabilities between states
enter as a parameter, which may be a function of temperature. In order
to make the physical model complete, we obtain the temperature dependence
of this parameter from simple arguments based on kinetics of collisions.

TIME-DEPENDENT ISING MODEL

The model to be used for the binary liquid mixture is the following:
Consider a lattice with n sites, each of which is occupied by either a
molecule of type A or one of type B. Let m_i = +1 or -1 according to
whether the site i is occupied by type A molecule or by type B. The
"system of interest" S is the Ising model interaction of these molecules
plus the thermal average energy E_j of independent molecules.

$$(1) \quad \mathcal{H} = \frac{J}{2} \sum_{j=1}^{n} \sum_{\delta=1}^{\ell} m_j \, m_{j+\delta} + \sum_j E_j \, , \qquad J \equiv J_{AA} + J_{BB} - 2J_{AB} < 0$$

where δ refers to nearest neighbors. The thermal environment consists of a
large number N of other interacting molecules of types A and B, where
$N \gg n \gg 1$, and all kinetic energies of molecules not contained in (1).
The system S and the environment interchange particles via an explicit inter-
action Hamiltonian. In a model for a ferromagnet the same Hamiltonian and
model could be used, except that the symbols have a different well-known
physical interpretation. This is also true for the one-component lattice
gas model for the liquid-gas transition. For the antiferromagnet only the
sign of J need be reversed. We shall for the sake of definiteness always
have in mind the binary liquid case.

In a previous[14] paper, a master equation for an Ising system was
derived.[15] The equation for the probability distribution P(m) describing
the system S, adapted to the binary liquid, is:

$$(2) \quad \frac{dP(m)}{dt} = \sum_{j=1}^{n} f(\omega_j) \left[e^{-\frac{\beta \omega_j}{2}} P(\bar{m}_j \div m_j) - e^{\frac{\beta}{2} \omega_j} P(m) \right]$$

where $P(m) \equiv P(m_1 \ m_2 \ \ldots m_n, \ t)$ is the time dependent probability that

the system S is in the state $|m\rangle = |m_1 \ m_2 \ \ldots m_n\rangle$; similarly

$P(\bar{m}_j, -m_j)$ is the probability of the state $|\bar{m}_j, -m_j\rangle$ which differs

from $|m\rangle$ only in that the type of molecule occupying the site j has

changed. In (2) $\beta = (kT)^{-1}$ and $w_j = 2m_j \left(\sum_s J \, m_{i+s} - \eta \right)$ with

$$\eta = \mu_A - \mu_B + kT \log \frac{q_A}{q_B}$$

where μ_A is the chemical potential, and q_A the non-configurational

partition function of an A molecule (In the ferromagnetic problem

$\eta = \gamma H$, where H is the magnetic field). The quantity $f(w)$ has the

property

$$(3) \qquad\qquad f(\omega) = f(-\omega)$$

and may be regarded either as a transition probability per unit time, or

as a spectral density characterizing the thermal reservoir. It is noted

that (2) is specialized also in that only transitions in which the occupation

of one site is changed at a time are considered; thus transitions in which an

A and a B molecule within S exchange places, or rearrangements involving the

change of many of the m_j simultaneously are not included in (2). However

the effects of such processes will be discussed also.

Another feature of (2) is that the function $f(w)$ is assumed independent

of j, so that all n sites of S are treated as equivalent, regardless of

whether the site lies on the surface or in the interior of the region S.

This assumption is strictly true if S is arranged in a two-dimensional

sheet with periodic boundary conditions, but is at best only a useful

approximation for other geometries. For the sake of clarity we shall

regard the present formulation as a theory for the relaxation of the two-

dimensional Ising model.

Further η will be put equal to zero, implying $\langle N_A \rangle = \langle N_B \rangle$, which is just the critical mixture of A and B molecules, according to the Ising model.

APPROXIMATE SOLUTIONS

While one can give the exact formal solution of (2), the explicit evaluation of the formal solution appears to be very complicated. Here we give only two types of simple approximate solutions for the first moment: First a solution in the molecular field approximation and secondly a solution obtained as an expansion in powers of tanh $J\beta$. From (2) and (3) one has[13] [14] the equation for $\langle m_j \rangle = \sum_j m_j \, P(m,t)$

$$(4) \qquad \frac{d \langle m_j \rangle}{dt} = - \langle m_j f(\omega_j) \, e^{\frac{\beta}{2} \omega_j m_j} \rangle$$

The molecular field approximation consists of replacing m_ℓ , for $\ell \neq j$, in (4) by $M = \langle m_j \rangle$. Pertinent features of this approximation are: (i) It can give only the relaxation of the uniform mode, because of the $\langle m_j \rangle = \langle m_\ell \rangle$ assumption. (ii) Had processes consisting of exchange of position among molecules within S, been included in (1), they would not have contributed to the relaxation anyway. (iii) The approximation is not restricted to any particular temperature range. Let $\mathcal{E} = \delta |J| M$, where δ is the number of nearest neighbors. Then (4) becomes

$$(5) \qquad \frac{d\mathcal{E}}{dt} = - f(\mathcal{E}) \cosh \beta \mathcal{E} \left[\mathcal{E} - \delta |J| \tanh \beta \mathcal{E} \right]$$

which corresponds to critical behavior at $T = T_c = \dfrac{\delta |J|}{k}$. Thus for a critical mixture of the two liquids ($\eta = 0$) the relaxation rate is according to (5) proportional to $\left[M - \tanh \beta \delta |J| M \right]$. It is seen from Fig. (1) that this quantity becomes extremely small near

$T = T_c$, especially for small values of M corresponding to the long decay times (narrow line) observed in the experiment. For $T \gtrsim T_c$ and small M, the decay is according to (5) exponential (and the line Lorentzian) with decay time $t_R \sim (T-T_c)^{-1}$, if $f(\epsilon)$ remains finite at the critical temperature. The well-known slowness of the approach to equilibrium in the neighborhood of the critical point is seen to follow already from the detailed balancing condition implicit in (2). In the experiments [4] [6] one does not usually observe the relaxation of the uniform ($\vec{k}=0$) mode, but rather that of long but finite wavelengths. The data does however indicate a Lorentzien line shape and extreme narrowing for scattered radiation for sufficiently small k as $T \rightarrow T_c$ from above, apparently consistent with (5). However, as will be shown later on, the long relaxation times are not to be ascribed to the detailed balancing condition alone, but also to the temperature dependence of the $f(\epsilon)$.

We now proceed to solution of (2) by a different approximation, expansion in powers of $a \equiv \tanh \beta |J|$. Features of this approximation are: (i) The relaxation of a standing concentration wave with arbitrary wave vector can be evaluated. (ii) The approximation is best for high temperatures. Since there exists a small expansion parameter, it is a systematic expansion. Note however that $a < 1$ even at the critical point. (iii) "Exchange" processes do effect the solution. Further in (2), the quantity $f(w_j)$ will be approximated by $f(0)$ independent of the m_j. The physical meaning of this step is the following: $f(w_j)$ is a transition probability per unit time, and can be written as a spectral density of a correlation function of variables involving the heat bath coordinates only. In particular they involve the molecular velocities. If the correlation times which characterize the functions of velocities are short compared to $[\gamma |J|]^{-1}$ then indeed

$f(\omega_j) \cong f(0)$. Let $\lambda = 2f(0)[\cosh\beta J]^{\gamma}$. Then (4) becomes

$$(6) \qquad \frac{d\langle m_j \rangle}{dt} = -\lambda \left\langle m_j \prod_{\delta=1}^{\gamma} (1 - m_j m_{j+\delta}\, a) \right\rangle$$

The equations for higher moment can be obtained[13] [14] from (2)

$$(7) \qquad \frac{d}{dt}\left\langle \prod_{i=1}^{r} m_{q_i} \right\rangle = -\lambda \left\langle \left(\prod_{i=1}^{r} m_{q_i} \right) \sum_{j=1}^{r} \prod_{\delta=1}^{\gamma} (1 - m_{q_j} m_{q_{j+\delta}}\, a) \right\rangle$$

Here the $q_1, q_2 \cdots q_r$ designate a particular set of lattice sites. Dropping all terms in (6) which are of order a^2, and introducing $m(\vec{k}) = \sum_j e^{i\vec{k}\cdot\vec{j}} m_j$ yields for $a^2 \ll 1$

$$(8) \qquad \frac{d\langle m(\vec{k})\rangle}{dt} = -\lambda \langle m(\vec{k})\rangle [1 - \gamma(\vec{k})a] + \theta(a^2)$$

where $\gamma(\vec{k}) \equiv \sum_\delta e^{i\vec{\delta}\cdot\vec{k}}$ A Fourier component with wave vector $\vec{k}$, will decay with relaxation time

$$(9a) \qquad \frac{1}{\tau(\vec{k})} = \lambda\left[1 - \gamma(\vec{k})a \right]$$

For long wavelength $|\vec{k}\cdot\vec{\delta}| \ll 1$ one has

$$(9b) \qquad \frac{1}{\tau(\vec{k})} = \lambda[1 - \gamma a] + \lambda \sum_\delta (\vec{\delta}\cdot\vec{k})^2$$

the quadratic dependence of $[\tau(\vec{k})]^{-1}$ on $\vec{k}$ implies that for light scattered through an angle θ, the scattered line is broadened[9] proportionally to $\sin^2\frac{\theta}{2}$, in agreement with experiments for small angle scattering.[4] [6] The uniform mode $(\vec{k}=0, \psi=0)$ relaxation time becomes infinite according to (9b) at $\gamma a = 1$. This point is somewhat above the exact (Onsager) critical point. Presumably if the coupled equations (6) and (7) were solved to all orders in a, the singular point would be the exact critical point. When (6) and (7) are solved to higher order[16] then linearly in a, one obtains a decay in as a sum of exponential terms, only some of the relaxation times will become infinite at the critical point, while others remain finite.

PHYSICAL INTERPRETATION

The quantity $\langle m_j \rangle = n_j^A - n_j^\beta$, is the difference between the expected number of A molecules at site j and the expected number of B molecules. Since $n_j^A + n_j^\beta = 1$, one also has $\langle m_j \rangle = 1 - 2n_j^\beta = 2n_j^A - 1$. This measure of concentration is expanded in a Fourier series, yielding independently decaying Fourier components to first order in a according to (9); however the terms $\sim a^2$ couple the different Fourier components.

Now we must consider the temperature dependence of the parameter λ or rather the transition probability per unit time $f(0)$, in order to have a complete model of the critical behavior. If the transition between states $|m\rangle$ and $|\overline{m}_j, -m_j\rangle$ are due a perturbation Hamiltonian of the simple and plausible form $\mathcal{H}'_j = (a_j \sigma_j^+ + a_j^+ \sigma_j^-)$, where the a_j is an operator containing the variables of only the environment (i.e. not those of the System S), and $\sigma_j^\pm = \sigma_j^x \pm i\sigma_j^y$, then[14] [17] if $\langle a_j \rangle_\beta = 0$

(10) $\quad f(0) = f_j(0) = \pi \, \mathrm{Re} \int_{-\infty}^{\infty} \langle a_j(\tau) a_j^*(0) \rangle_\beta \, d\tau$

where $\langle \ \rangle_\beta$ means thermal average. The operator a_j can depend on all velocities and on the arrangement of molecules in the environment. Suppose a_j can be written as a product $\quad a_j = \alpha \cdot g$ where α depends on the arrangement of A and B molecules in the neighborhood of j, and g depends on velocities of molecules in that neighborhood. Further we take α and g to be statistically independent, and the correlation time for g to be much shorter than that for the α. Then

(11) $\qquad f(0) \simeq \pi \, \langle |\alpha(0)|^2 \rangle_\beta \int_{-\infty}^{\infty} \langle g(\tau) g(0) \rangle_\beta \, d\tau$

The process described by $f(0)$, i.e. by $\mathcal{H}_j$, namely the replacement of a A molecule at site j by a B molecule from the environment is the less likely, the fewer the B molecules there are in the neighborhood. Suppose that in the binary liquid clusters ("drops") of A and B are formed of average radius $\nu\delta$ where δ is the lattice spacing, and the rate at which a molecules jumps from one site to the next is C. Then the A molecule will on the average have to travel a net distance of the order of $\nu\delta$ to replace a B molecule, which according to the elementary theory of the random walk requires on the average ν^2 steps or traveling a total distance $\nu^2\delta$. Consequently the transition rate for the process in question has besides the velocity dependence a factor $\langle |\alpha(0)|^2 \rangle_\beta \sim \delta \cdot c \, (\nu\delta)^{-2}$. The distance $\nu\delta$ can be evaluated from the correlation function for the equilibrium Ising model [18]

(12) $\qquad \langle m_j m_\ell \rangle \simeq \dfrac{e^{-\kappa\delta|j-\ell|}}{\delta|j-\ell|} \quad , \quad \kappa^2 = \dfrac{\mathrm{const}}{\chi}$

Where $\chi \equiv \left(\dfrac{\partial \langle m_j \rangle}{\partial \eta} \right)_{\eta=0}$ is the analog of the magnetic

susceptibility for a binary liquid mixture.　　　(11) becomes

$$(13) \quad f(0) \cong \frac{const}{\chi} \int_{-\infty}^{\infty} \langle g(r) g(0) \rangle_{\beta} dr$$

To be even more explicit one may take g to be a Taylor series in
velocities, and keep the leading (linear) term. Presumably a process
involving only two molecules (one type A molecule and one B molecule) depends
primarily on the resulting velocity correlation function, rather than those
containing products of three or more velocities. In fact the correlation
between an A velocity and a B velocity is what is important. For our
purposes, it is sufficient to require that $\int_{-\infty}^{\infty} \langle g(r) g(0) \rangle_{\beta} dr$
is a slowly varying function of temperature, and finite near T_c.
However for the Ising model $\chi^{-1} \xrightarrow[T \to T_c]{} const \, (T-T_c)^{5/4}$.
The relaxation time (9b) may then be written as

$$(14) \quad \frac{1}{\tau(\vec{l})} \cong \frac{A}{\chi} \left[1 - \gamma a \right] + \frac{\mu}{\chi} \sum_{\delta} \left(\vec{\delta} \cdot \vec{l} \right)^2$$

where A is a slowly varying function of T near Tc.
According to (14), $\tau(\vec{l})$ has the same singular behavior as χ
in the critical region, except that for $\vec{l} = 0$, it diverges still more
rapidly. Again (14) is consistent with present experiments.

In order to see the relation of the present model to the theory
of Debye[9] based on the diffusion equation, retain only the linear term
in (6)

$$(15) \quad \frac{d\langle m_j \rangle}{dt} = \frac{Aa}{\chi} \sum_{\delta} \left[\langle m_{j+\delta} \rangle - \langle m_j \rangle \right] + \frac{A}{\chi} \left[\gamma a - 1 \right] \langle m_j \rangle$$

which is a finite difference equation corresponding to the diffusion
equation

$$(16) \quad \frac{\partial \langle m \rangle}{\partial t} = D \nabla^2 \langle m \rangle - \frac{\langle m \rangle}{\tau}$$

with $\quad D = \chi^{-1} A a \delta^2 \quad$ and $\quad \tau^{-1} = \chi^{-1} A (1 - \gamma a)$.

The $\langle m \rangle / \tau$ term is absent in the Debye treatment[9]. The expression for the diffusion constant is usually obtained[19] in a formal way from the theory of linear irreversible processes; in particular the factor $\chi = \left(\frac{\partial \langle m \rangle}{\partial \eta} \right)_{\eta=0}$ arises from the changing of variables from the thermodynamic force η to the variable $\langle m \rangle$. Moreover in the linear theory $A a \delta^2$ becomes precisely a velocity-correlation function.

We have not considered the possible mechanism of an A and B molecule within S exchanging places. If consider such processes must add to the right-hand side of (2) the terms

$$(17) \quad \sum_{j < \ell} \lambda_{j\ell} \delta_{m_j, -m_\ell} \left[e^{-\frac{\beta}{2}(\omega_j + \omega_\ell)} P(\overline{m}_{j\ell}, -m_j, -m_\ell) - e^{\frac{\beta}{2}(\omega_j + \omega_\ell)} P(m) \right]$$

The Kronecker delta assures that the two sites (j, ℓ have a different occupation, so that the process can take place. Consequently the clustering tendency is explicitly taken into account, and the $\lambda_{j\ell}$ will **not** vanish at the critical point. Using the relation $\delta_{m_j, -m_\ell} = \frac{1}{2}(1 - m_j m_\ell)$ one can again find moment equations.

The equation for the first moment is

$$(18) \quad \frac{d \langle m_k \rangle}{dt} = - 2 \cosh(2\beta J) \sum_{\delta} \lambda_{k, k+\delta} \left\langle (m_k - m_{k+\delta}) e^{\frac{\beta}{2}(\omega'_{k+\delta} - \omega'_k)} \right\rangle$$
$$- 2 \sinh(2\beta J) \sum_{\ell} \sum_{\ell+\delta} \lambda_{\ell, \ell+\delta} \left\langle (m_k m_\ell m_{\ell+\delta} - m_k) e^{\frac{\beta}{2}(\omega'_\ell + \omega'_{\ell+\delta})} \right\rangle$$
$$- 2 \sum_{\ell} \lambda_{\ell k} \left\langle (m_k - m_\ell) e^{\frac{\beta}{2}(\omega_\ell + \omega_j)} \right\rangle$$

where $\ell \neq k$ and $\omega'_s + \omega'_{s+\delta} \equiv \omega_s + \omega_{s+\delta} - 4 J m_s m_{s+\delta}$.

At high temperatures, $|\beta \delta J| \ll 1$, the right hand side of (18) yields simple diffusion terms. But already to first order in a , contributions to $\frac{d \langle m_k \rangle}{dt}$ arise which depend on correlation between three sites. In particular the second term in (18), which involves

an interchange between sites ℓ and $\ell + \delta$,but not a direct exchange with k itself (unless $\ell + \delta = k$) will contribute.

CONCLUDING COMMENTS

To summarize, we have attempted to give a simple microscopic model for the relaxation of concentrations near the critical point in a binary liquid mixture. Transition probabilities between states are taken to be independent of the m_j, except for the dependence required by detailed balancing. If consider processes for which only the occupation of one site in S is changed then from this condition alone follows that the k = 0 mode has an infinite relaxation time at $T = T_c$, and inverse relaxation times for small finite k vary as k^2 (equations 9). Further consideration of the dependence of the transition probability on the tendency of each molecule to surround itself with molecules of its own type near T_c, leads to (14), indicating a vanishing of $[\tau(\vec{k})]^{-1}$ for all k at the critical point, to first order in $\tanh \beta |J|$. In the same approximation a diffusion equation is obtained; such a diffusion equation (without however the relaxation term) is the starting point of Debye's phenomenological theory. However already to order $(\tanh \beta J)^2$ it is not sufficient to deal only with (6) or a diffusion equation, but the coupling to some of the equations (7) for higher order correlation functions must be considered; to put it differently, the Fourier components $\langle m(\vec{k}) \rangle_t$ no longer relax independently of each other at the lower temperatures.

For processes consisting of the exchange of location of an A and a B molecule within S, we find that the diffusion model already breaks down to first order in $\tanh \beta |J|$. It is conceivable that still more complicated processes involving two, three or more sites within S contribute to the relaxation. We have not considered such processes.

It was already noted that the single relaxation time for $m(\vec{\ell})$ at small a goes over into several relaxation times when terms of order a^2 (or even of order a according to (18)) are considered: $\langle m(\vec{\ell})\rangle_t = \sum_s A_s\, e^{-t/\tau_s(\vec{\ell})}$. Now the A_s are linear combination of suitably averaged initial values of the various moments. Only some of the τ_s^{-1} will vanish at the critical point, the others remaining finite. Which of the relaxation times dominates in the critical region will depend on the state of the system at $t=0$. Of the whole spectrum of relaxation times contained in the master equation, certain ones may dominate the relaxation of $\sum_{j=1}^{m}\langle m_j\rangle$. Another set may dominate the relaxation of particular high-order correlation functions. These points are mentioned, because the possibility suggests itself that the observed vanishing of $[\tau(\vec{\lambda})]^{-1}$ as $T\to T_c$ in many experiments [4) 5) 6)] might thus be reconciled with the non-vanishing $[\tau(\vec{\ell})]^{-1}$ found in ferromagnets[7)].

ACKNOWLEDGEMENT:

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REFERENCES

1. L. Onsager, Phys. Rev. 65, 117 (1944); C. Domb, Advan. Phys. 9, nos. 34, 35 (1960)

2. M. E. Fisher, J. Math Phys. 4, 278 (1963)

3. C.N. Yang and T. D. Lee, Phys. Rev. 87, 404 (1952); 87, 410 (1952)

4. S. Alpert, Y. Yeh, E. Lipworth, Phys. Rev. Letters 14, 486 (1965)

5. P. Heller Conference on Phonomenar in the Neighborhood of Critical Points, Washington D.C. (April 1965)

6. S. Alpert, D. Balzarini, R. Novick, L. Siegel and Yeh (preprint) N. Ford and G. Bendek, Phys. Rev. Letters 15, 649 (1965)

7. Passell, Blinowski, Brun and Nielson, Phys. Rev. 139. A1866 (1965)

8. The exceptions are the neutron scattering experiments on ferromagnets (ref. 7). They do not yield the extremely long critical relaxation times.

9. D. Debye, Phys. Rev. Letters 14, 783 (1965)

10. The liquid-vapor critical behavior is described by the Landau-Plaszeh theory based on linearized hydrodynamics, Phys. Z. der Soviet Union 5, 172 (1934), recently reviewed by R. D. Mountain (preprint)

11. For magnetic systems see H. Mori and K. Kawasaki, Prog. Theor. Phys. 27, 529 (1962) and T. Moriyer, Prog. Theor. Phys. 28, 371 (1962)

12. T. Tanaka and P. Meijer, J. of Phys.-Soc. Japan 17, Supp. BI, 78 (1962)

13. R. Glauber, J. Math. Phys. 4, 294, (1963). As Glauber points out, his master equation is based on a stochastic model and does not follow from the Liouville equation. The present model is under well-defined conditions derivable from the Liouville equation. Thus our master equation has a more satisfactory foundation; however it is more difficult to solve than Glauber's equation.

14. S. P. Heims, Phys. Rev. 138, A587 (1965)

15. Equation (2) and (3) are a particular case of the Pauli equation specialized to the case of a relatively small system in contact with a large thermal reservoir. There exist various sets of conditions for which this equation can be derived; Ref. 14 gives one set of sufficient conditions. Alternative derivations require the smallness of the coupling between S and the environment, relative to the total energy of the system of n + N particles, as the essential condition: A. Sher and H. Primakoff, Phys. Rev. 119, 178 (1960); E. Montroll in Lectures in Theoretical Physics III, Univ. of Colorado Summer School (1960), edited by W.E. Brittin, B.W. Downs and J. Downs (Inter-science Publishers, Inc. New York 1961).

REFERENCES

16. A calculation to order a^2 verifies that the point at which $[\tau(\omega)]^{-1} \to 0$ is closer to the exact critical point than that given by (9b). According to (9b) also $[\tau(\tau)]^{-1} \to 0$ at some point below T_c. However since the calculation neglects terms of order a^2, this result for $T < T_c$ cannot be taken seriously.

17. A. Abragam Principles of Nuclear Magnetism, Clarendon Press (1961) If other forms of $\mathcal{H}'$ are considered in which $m_i \to - m_i$ and nothing else changes, still an expression for $f(o)$ of the same general form as (10) would apply.

18. R. H. Brout, Phase Transitions, pp. 20-22, W. Benjamin Inc. (New York 1965)

19. R. Kubo, J. Phys. Soc. Japan 12, 570 (1957) M.S. Green. J. Chem. Phys. 22, 398 (1954)
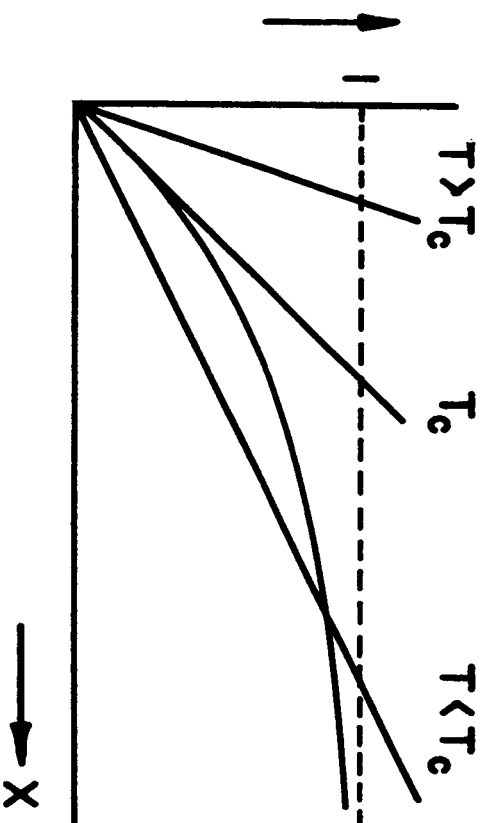
Fig. I Graph of tanh x and of $C = \dfrac{2kT}{Z|J|}$

for various T.

$T > T_c$

T_c

$T < T_c$

X

1